CHAPTER VIII

STUDIES ON GROWTH AND ETCH FEATURES OF ANTIMONY CRYSTALS GROWN FROM VAPOUR

This work was taken up for a comparison of the behaviour of the crystals grown from melt and vapour. The following aspects are included:

(1) To observe whether the crystals grown from the vapour exhibit any preferred orientation;

(2) To study etching of vapour grown crystals with various reagents and compare the results with the melt grown crystals;

(3) To study the general surface topography with special interest to the observation of growth spirals, which have not been reported so far.

The author wishes to point out that the results are presented very briefly and the details which are common to both melt grown and vapour grown crystals are omitted. Regarding the surface topography, a large number of surface features has been observed and the results are presented, but in many cases no theoretical explanation has been offered.

The apparatus used for growing crystals has been described in Chapter IV. No measurements have been made on the supersaturation in the growing system but increase of supersaturation at the vapour-solid interface within the system is assumed when the rate of lowering the temperature of the system is increased. The crystal nucleation takes place (i) at the walls of the silica tube, (ii) at the end of the graphite crucible and (iii) at the top of the graphite cover of the crucible. Crystals are carefully removed from these places after the system cools down to room temperature. The results of the experiments can be summarised as follows:

(1) When the rate of cooling is small $\approx 1°C/min.$, the crystals are comparatively large having triangular facets of 1 to 3 mm. size. In addition to this a few hexagonal facets are also obtained.

(2) When the rate of cooling is increased to 2-5°C/min. the size of the crystals reduces and a greater number of crystals having hexagonal facets are obtained.

(3) For large cooling rates, rapid sublimation takes place and a thick layer of antimony is deposited along the walls of the tube. No crystals are obtained in this case.

The triangular faces are evidently the (111) planes. One such face is shown in Fig. 1. It is observed that the faces contain a large number of small triangular features which are oriented opposite to those of the crystal itself. A photomicrograph at higher magnification is shown in Fig. 2. The profile shift indicates that these are elevations. In order to study whether these are surface or body features of the crystal, the crystal has been etched in a solution of tartaric acid and nitric acid, i.e., reagent E mentioned in Chapter VI on etching of melt grown crystals. It is seen from Fig. 3 that the growth features have disappeared and etch figures have been formed on the surface. This suggests that the triangular features on the faces are surface features and are formed at dislocation sites. It can reasonably be concluded that these oriented overgrowth (111) facets at dislocation sites are formed by deposition of vapour towards the end of the growth. Similar observations have been reported by Pandya et al[1] on antimony, by Arizumi et al[2] on germanium and by Crocker[3] on gallium arsenide. Yamanak et al[4] have observed triangular patterns on surfaces of zinc selenide grown from vapour.

A unique spiral observed is shown in Fig. 4. The spiral has a large step height as indicated by the light

Fig. 1 X 90

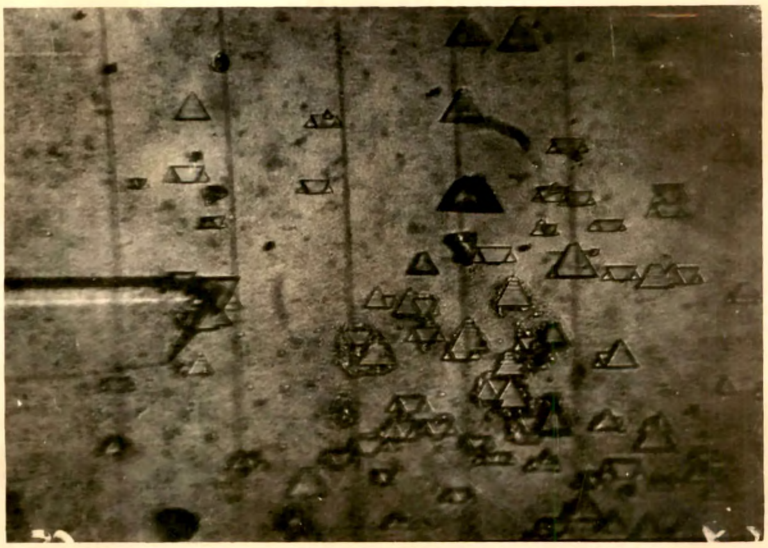

Fig. 2 X 360

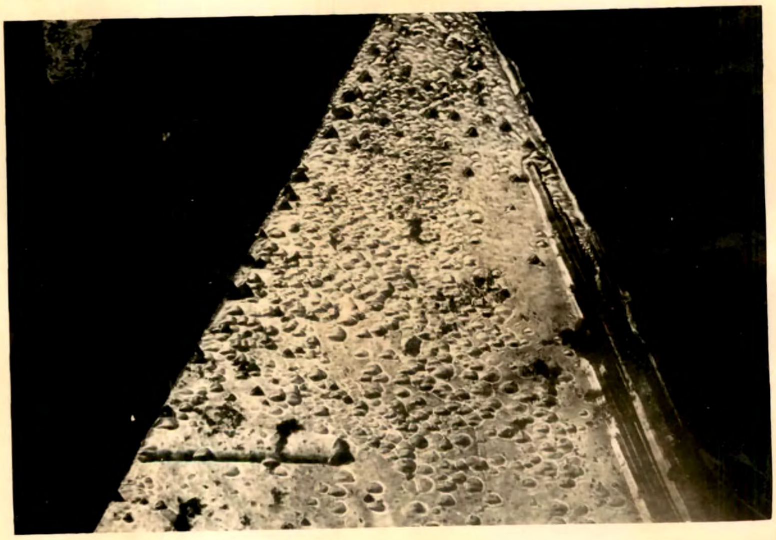

Fig. 3 X 90

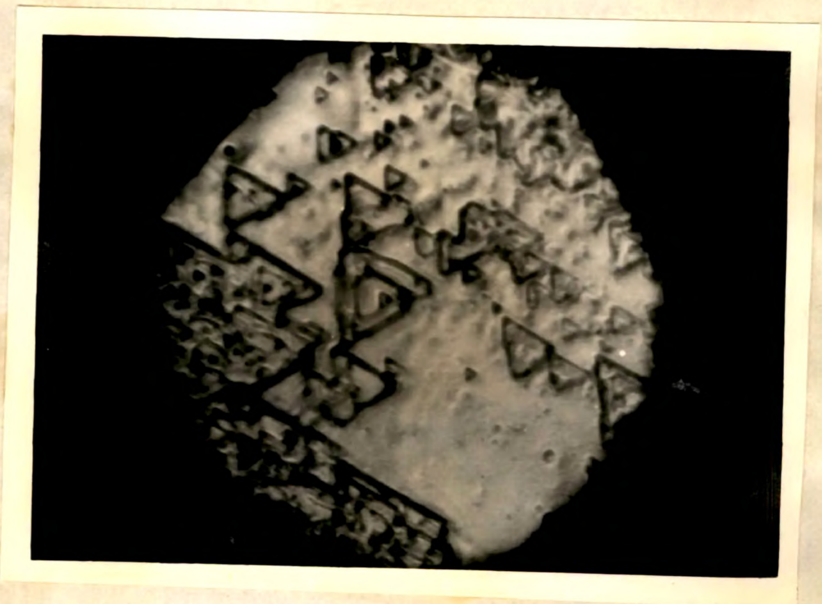

Fig. 4 X 360

profiles running across it, shown in Fig. 5. In order to find out whether this spiral is due to dislocation or not, the surface is etched and the results are shown in Fig. 6. It is observed that a number of pits have been formed in this region. This suggests that the spiral is the result of a number of interacting dislocations. It is not possible to find out whether these pits are due to screw dislocations or edge dislocations. However, if they are due to screw dislocations, it will agree well with Frank's theory that interacting dislocations can give rise to large step height of spirals. If this be so, the pits indicate that screw dislocations can also be revealed by etching. If these pits are due to edge dislocations, then one can conclude that spirals can be formed as a result of interaction of edge dislocations also.

Fig. 7 is a photomicrograph showing a partial polygonal spiral with a light profile running across it. A complex pattern consisting of two or three interacting polygonal spirals is shown in phase contrast in Fig. 8. Fig. 9 is a surface of the crystal showing (A) a terraced growth pyramid, (B) a normal growth pyramid with a few steps at the bottom layers and (C) a growth pyramid with a flat terrace.

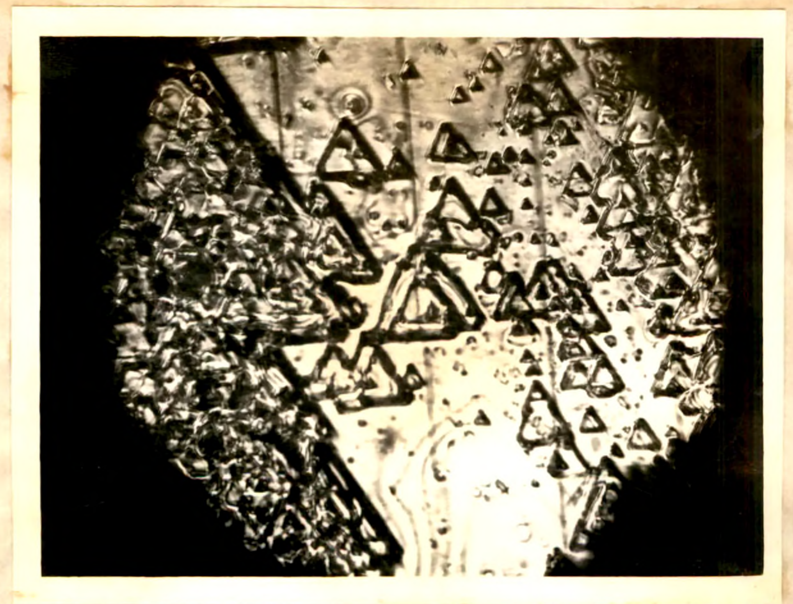

Fig. 5 X 360

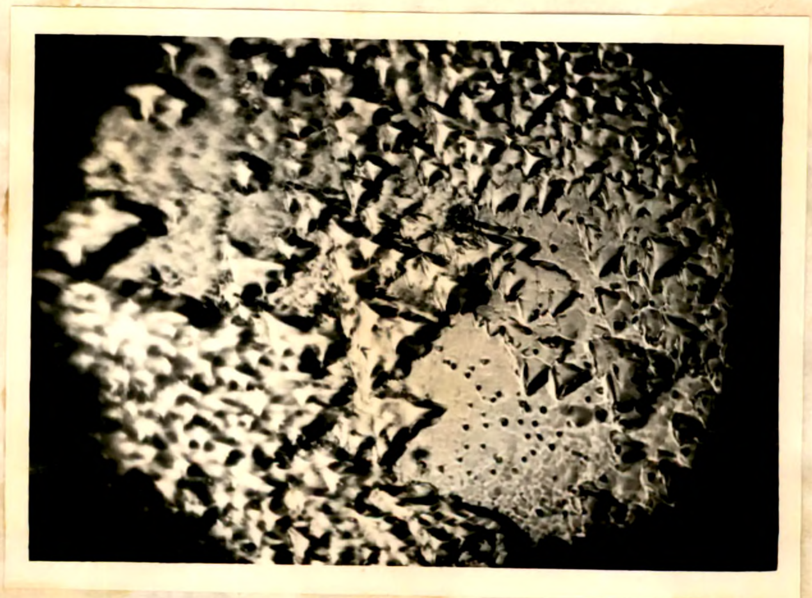

Fig. 6 X 360

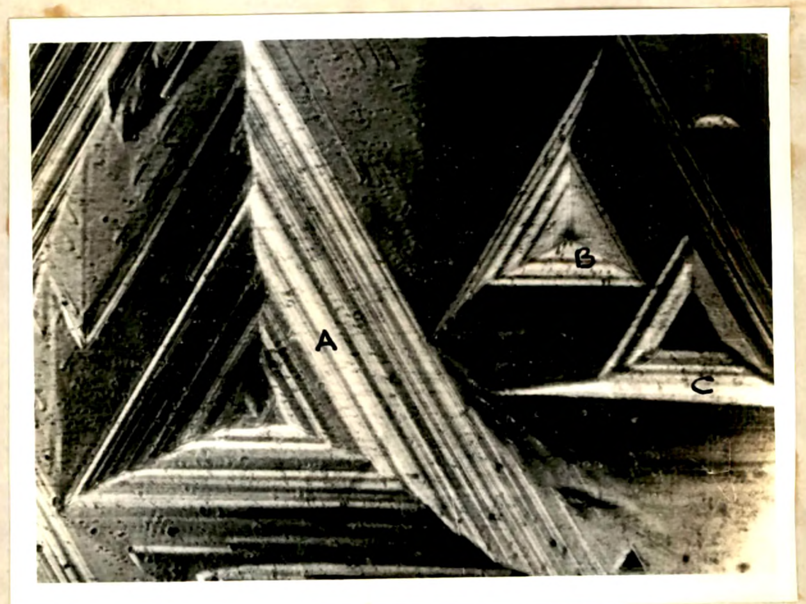

Fig. 9 X 90

Fig. 10 is a hexagonal facet obtained when the rate of cooling is in the range 2-5°C/min. The surface after etching is shown in Fig. 11. The growth facet shows a few growth triangles oriented in the same manner as the face itself. This is contradictory to the observations in Figs. 1-3. However, the etched surface clarifies this point well. One can see the crystal boundary running in a vertical direction, in addition to the boundaries at the bottom. This shows that the hexagonal facet is a composite of a large number of planes, most of them being (111), which probably might have nucleated at different points and finally joined together. The existence of triangular etch pits on some of these planes establishes that these are the (111) planes.

Another hexagonal face after etching is shown in Fig. 12. It is seen that while one face shows triangular etch pits, low angle boundaries, etc., the other face does not show any etch figure at all. This shows that the etchant used can reveal dislocations only on the (111) cleavage planes.

At higher rates of cooling, in addition to the hexagonal facets, complex triangular patterns, as in

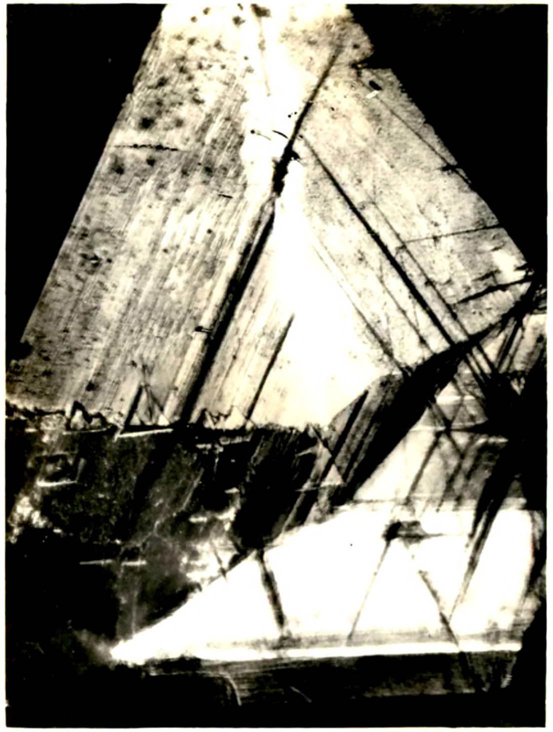

Fig. 10 X 90

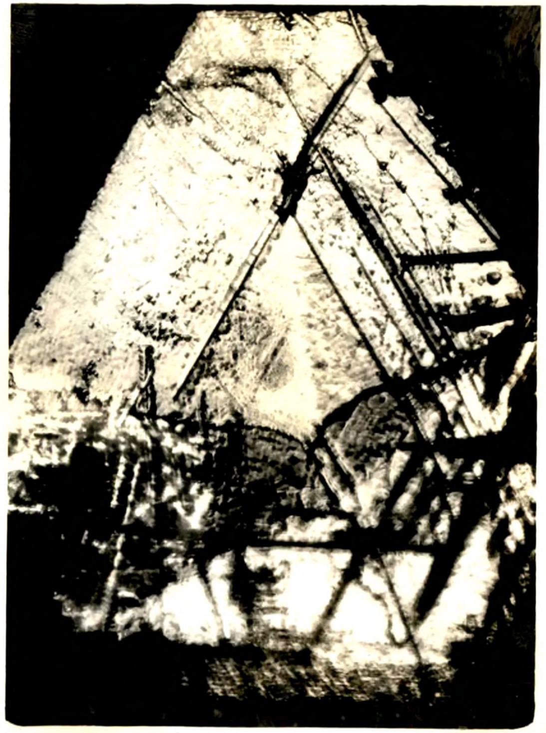

Fig. 11 X 90

Fig. 12 X 170

Fig. 13, are also observed. Etching of such crystals with CP-4 - A reveals a block pattern shown in Fig. 14, while Fig. 15 is an interferogram on such a structure. The pattern is similar to those observed by Pandya and others[5-7] on diamond, calcite and bismuth and is due to prolonged etching of the surface. These are all triangular pits as seen from the interferogram.

Some surfaces show a number of parallel striations, as shown in Fig. 16. Fig. 17 is an interferogram of the surface of Fig. 16; Fig. 18 being the surface after etching. Parallel rows of etch pits along the striation boundaries suggest that these are tilt boundaries.

In addition to these, surfaces also show a pattern shown in Fig. 19. It appears that the surface may be a (100) plane with (100) facets grown by a similar mechanism. The 'stepped nature' of the surface is evident from Fig.20. However, on etching it is observed that triangular etch pits are formed along the step boundaries and at random (Fig.21) This proves that the surface is again a (111) plane.

Thus the crystals grown from vapour have the (111) faces developed, or, in other words, the growth proceeds

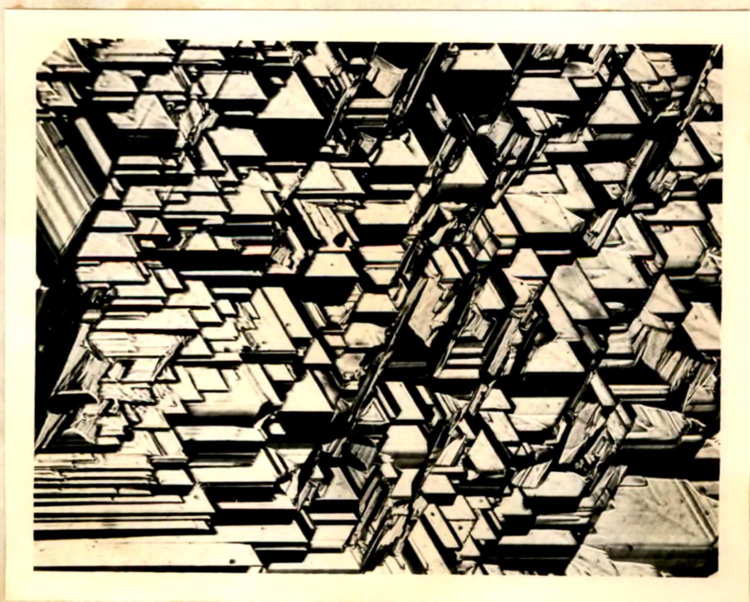

Fig. 13 X 110

Fig. 14 X 450

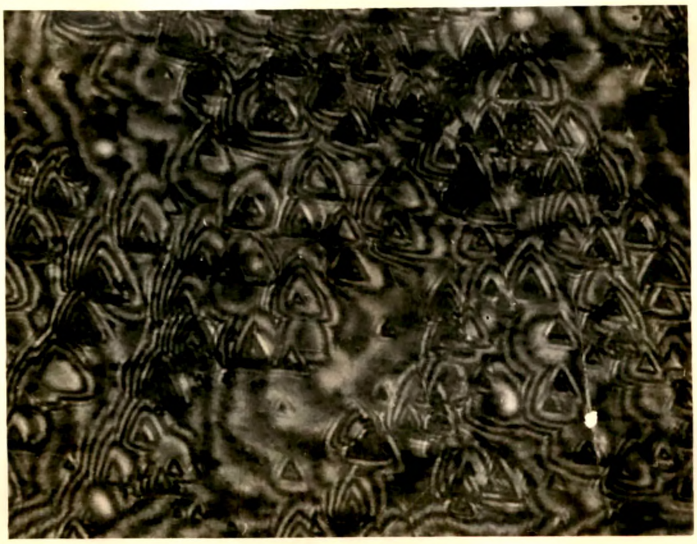

Fig. 15 X 340

Fig. 18 X 360

Fig. 19 X 90

Fig. 20 X 360

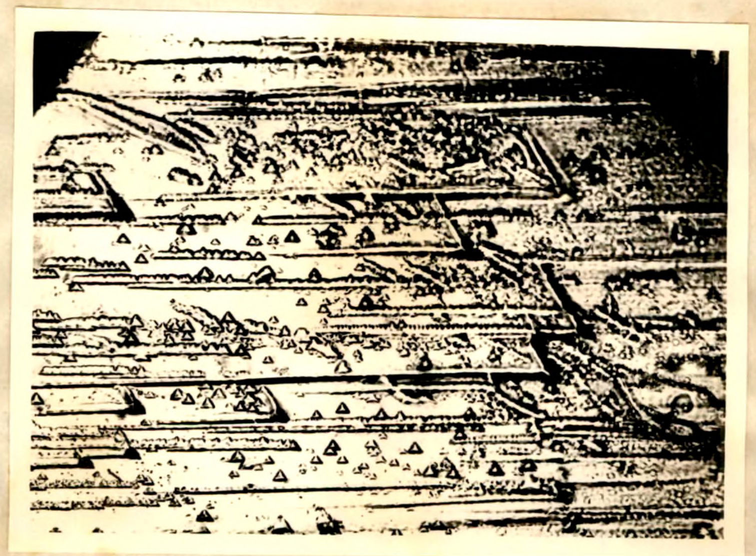

Fig. 21 X 170

preferentially such that the (111) plane, which is the plane of closest packing in antimony, is perpendicular to the growth direction. Within the range studied, no change in orientation is observed, the hexagonal facet which is found on a number of (111) planes is produced because of increased number of nucleation centres produced at higher supersaturations. Results are in conformity with Frank's theory of crystal growth. Differences have been observed with melt grown crystals where the orientation is found to vary. The cause of this difference may be due to the fact that in crystals growing from melt the thermal conduction plays a more important role and influences the orientation of the crystals.

Etching of vapour grown crystals gives results similar to those on melt grown crystals. The etchants normally used do not produce pits on planes other than the (111) plane.

CONCLUSIONS:

(1) Triangular and hexagonal facets are developed in vapour grown crystals.

(2) The latter is a complex of a number of (111) planes.

(3) Triangular facets show oriented growth patterns consisting of triangles oriented opposite to the face itself, which are formed at dislocation sites.

(4) In addition to terraced pyramids complex triangular patterns have been observed on the grown surfaces.

(5) A spiral with a large step height has been observed which has been shown to be produced by the interaction of a number of dislocations.

(6) Etch behaviour of the vapour grown crystals is same as that of the melt grown crystals.

(7) Evidences have been presented to show that etching reagents reveal dislocation pits only on (111) plane.

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